

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
4 July 2002 (04.07.2002)

PCT

(10) International Publication Number
WO 02/051892 A1

(51) International Patent Classification⁷: C08F 228/02, (74) Agents: FAGAN, Lisa, M. et al.; Office of Intellectual
220/30, G02B 1/04 Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(21) International Application Number: PCT/US01/14040

(81) Designated States (*national*): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PI, PT, RO, RU, SJ, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(22) International Filing Date: 1 May 2001 (01.05.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/746,613 21 December 2000 (21.12.2000) US

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

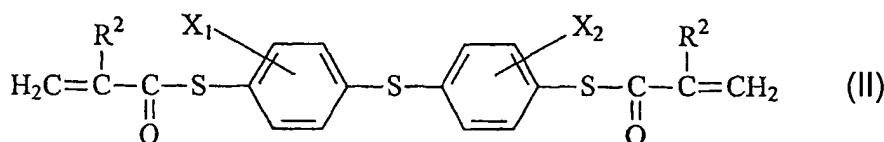
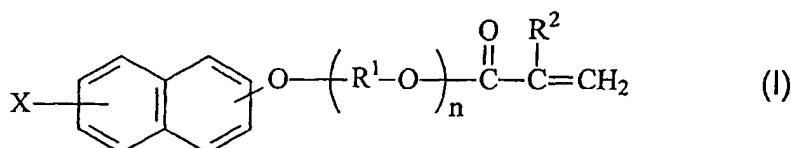
(71) Applicant: 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

Published:

— with international search report

[Continued on next page]

(54) Title: HIGH REFRACTIVE INDEX MICROREPLICATION RESIN



WO 02/051892 A1

(57) Abstract: A polymerizable composition that includes a monomer of the formula (I) wherein X is hydrogen or one or more of methyl, chlorine, bromine or iodine, R¹ is a straight or branched alkyl linking group of 2 to 12 carbon atoms, R² is hydrogen or methyl, and n is 1 to 3; and a monomer of the formula (II) wherein X₁ and X₂ are each independently hydrogen or one or more of methyl, chlorine, bromine or iodine, and R² is hydrogen or methyl is described having a high index of refraction and being suitable for use in forming an optical product.

WO 02/051892 A1



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

HIGH REFRACTIVE INDEX MICROREPLICATION RESIN

5

Technical Field

The invention relates to polymerizable compositions containing high index of refraction monomers, and to polymeric materials prepared therefrom. The invention also relates to optical products made from such polymeric materials.

10

Background

Optical materials and optical products are useful to control the flow and intensity of light. Examples of useful optical products include optical lenses such as Fresnel lenses, optical light fibers, light tubes, optical films including totally internal reflecting films, retroreflective sheeting, and microreplicated products such as brightness enhancing films (BEF) and security products. Examples of some of these products are described in U.S. Patent Nos. 4,542,449; 5,175,030; 5,591,527; 5,394,255 and others.

15

Optical products can be prepared from high index of refraction materials, including monomers such as high index of refraction (meth)acrylate monomers, halogenated monomers, and other such high index of refraction monomers as are known in the art.

20

See, for example, U.S. Patent Nos. 4,568,445; 4,721,377; 4,812,032; and 5,424,339.

25

The monomers can be cured or polymerized to take the form of a product capable of modifying or controlling the flow of light. In the particular structure of a microreplicated optical product, the monomers can be polymerized into a brightness enhancement film having a micro-fine prismatic pattern. See U.S. Patent Nos. 5,175,030 and 5,183,597. Brightness enhancement films are very useful in many of today's electronic products to increase the brightness of backlit flat panel displays such as liquid crystal displays (LCDs), electroluminescent panels, laptop computer displays, word processors, desktop monitors, televisions, video cameras, and automotive and avionic displays, among others.

30

One important property of an optical material is its index of refraction, because index of refraction is related to how effectively an optical material can control the flow of

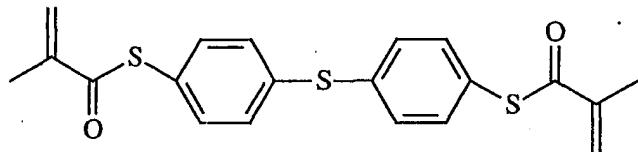
light. There exists a continuing need for optical materials and optical products that exhibit a high index of refraction.

With respect specifically to brightness enhancement films, the index of refraction is related to the brightness gain or "gain" produced by the brightness enhancement film.

5 Gain is a measure of the improvement in brightness of a display due to the brightness enhancement film, and is a property of the optical material, and also of the geometry of the brightness enhancement film. Typically, the viewing angle decreases as the gain increases. A high gain is desired for a brightness enhancement film because improved gain provides an effective increase in the brightness of a backlit display.

10 Improved brightness means that the electronic product can operate more efficiently by using less power to light the display. Reduced power consumption translates into reduced heat generation and therefore means increased component life. Thus, because of these advantages, there exists a continuing need to find optical products exhibiting improved index of refraction values.

15 Maruyama et al., U.S. Patent No. 5,183,917, describes the synthesis of a diphenyl sulfide of the formula:



20 This compound is described as having a high index of refraction. However, this monomer (4,4'-bis(methacryloyl thio)diphenyl sulfide, or MPSMA) is known to be a crystalline solid that is not very soluble in common acrylate monomers. Since a liquid composition is necessary to make a microreplicated product, MPSMA has had limited usefulness.

25 Fukushima et al., U.S. Patent No. 5,969,867, recognized the usefulness of MPSMA, but found it necessary to use bis(methacryloxyethoxyphenyl) propane and similar materials to solubilize the MPSMA. Unfortunately, these solubilizing materials have relatively low index of refraction values and thus it is difficult to produce compositions having index of refraction values above about 1.60 without using very high levels of MPSMA.

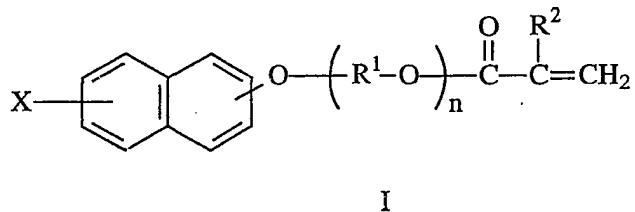
However, it is preferred to use lower levels of MPSMA due to its high cost and limited compatibility. In a particular example, Fukushima was able to obtain a composition with a refractive index of 1.65 that contained only 50 percent MPSMA by using a high level of phenyl thioethoxyethyl methacrylate. This material is not believed to be available commercially and is difficult to synthesize.

Thus, a need remains for improved polymerizable compositions having high index of refraction values using materials that can be easily synthesized using commercially available starting materials.

10

Summary

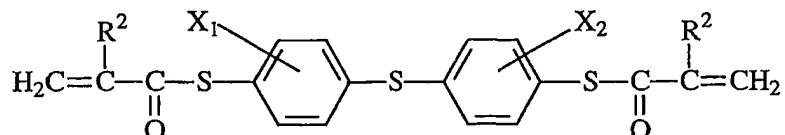
Accordingly, the invention is found in a polymerizable composition containing two monomers. The first monomer is of the formula I



15

where X is hydrogen or one or more of methyl, chlorine, bromine or iodine, R¹ is a straight or branched alkyl linking group of 2 to 12 carbon atoms, R² is hydrogen or methyl, and n is 0 to 3.

The second monomer is of the formula II



20

II

where X₁ and X₂ are each independently hydrogen or one or more of methyl, chlorine, bromine or iodine, and R² is hydrogen or methyl.

The invention is also found in an optical product having a base and an optical layer formed from the polymerizable composition described above. In another embodiment, the invention is also found in a microstructure-bearing optical product.

5

Brief Description of the Drawing

Figure 1 is a perspective view of an illustrative microstructure-bearing optical product of the present invention. This figure is not to scale and is not intended to be limiting in any manner.

10

Detailed Description

15

The present invention describes an optical product constructed of a base layer and an optical layer. The base layer can be of a nature and composition suitable for use in an optical product, i.e. a product designed to control the flow of light. Almost any material can be used as a base material as long as the material is sufficiently optically clear and is structurally strong enough to be assembled into or used within a particular optical product. Preferably, a base material is chosen that has sufficient resistance to temperature and aging that performance of the optical product is not compromised over time.

20

The particular chemical composition and thickness of the base material for any optical product can depend on the requirements of the particular optical product that is being constructed. That is, balancing the needs for strength, clarity, temperature resistance, surface energy, adherence to the optical layer, among others.

25

Useful base materials include cellulose acetate butyrate, cellulose acetate propionate, cellulose triacetate, polyether sulfone, polymethyl methacrylate, polyurethane, polyester, polycarbonate, polyvinyl chloride, syndiotactic polystyrene, polyethylene naphthalate, copolymers or blends based on naphthalene dicarboxylic acids, and glass. Optionally, the base material can contain mixtures or combinations of these materials. In an embodiment, the base may be multi-layered or may contain a dispersed phase suspended or dispersed in a continuous phase.

30

For some optical products such as microstructure-bearing brightness enhancement films, examples of preferred base materials include polyethylene terephthalate (PET) and polycarbonate. Examples of useful PET films include photograde polyethylene

terephthalate and MELINEXTM PET available from DuPont Films of Wilmington, Delaware.

Some preferred base materials can be optically active, and can act as polarizing materials. A number of bases, also referred to herein as films or substrates, are known in the optical product art to be useful as polarizing materials. Polarization of light through a film can be accomplished, for example, by the inclusion of dichroic polarizers in a film material that selectively absorbs passing light. Light polarization can also be achieved by including inorganic materials such as aligned mica chips or by a discontinuous phase dispersed within a continuous film, such as droplets of light modulating liquid crystals dispersed within a continuous film. As an alternative, a film can be prepared from microfine layers of different materials. The polarizing materials within the film can be aligned into a polarizing orientation, for example, by employing methods such as stretching the film, applying electric or magnetic fields, and coating techniques.

Examples of polarizing films include those described in U.S. Patent Nos. 5,825,543 and 5,783,120. The use of these polarizer films in combination with a brightness enhancement film has been described in U.S. Patent No. 6,111,696.

A second example of a polarizing film that can be used as a base are those films described in U.S. Patent No. 5,882,774. One example of such films that are available commercially are the multilayer films sold under the trade designation DBEF (Dual Brightness Enhancement Film) from 3M. The use of such multilayer polarizing optical film in a brightness enhancement film has been described in U.S. Patent No. 5,828,488.

This list of base materials is not exclusive, and as will be appreciated by those of skill in the art, other polarizing and non-polarizing films can also be useful as the base for the optical products of the invention. A short list of additional base materials can include those films described in U.S. Patent Nos. 5,612,820 and 5,486,949, among others.

One or more the surfaces of the base film can be optionally be primed or otherwise be treated to promote adhesion of the optical layer to the base.

The thickness of a particular base can also depend on the above-described requirements of the optical product. A thickness in the range of about 0.025 millimeters (mm) to about 0.5 mm is preferred, with a thickness in the range of about 0.075 mm to 0.175 mm is especially preferred.

The optical layer typically directly contacts the base layer, and can be of a size, shape and thickness allowing the optical layer to direct or concentrate the flow of light. Thus, the optical layer can be a flat film or the optical layer can have a structured or microstructured surface that can have any of a number of useful patterns. These include 5 regular or irregular prismatic patterns, an annular prismatic pattern, a cube-corner pattern or any other lenticular microstructure. A preferred microstructure is a regular prismatic pattern that can act as a totally internal reflecting film for use as a brightness enhancement film.

10 The optical layer is formed from a polymerizable composition that includes at least two monomers. Monomer (a) is a naphthyl monoacrylate while monomer (b) is a diphenyl sulfide dithio(meth)acrylate. Each of the monomers are described in greater detail hereinafter.

Definitions

15 "Refractive index" is defined herein as the absolute refractive index of a material (e.g., a monomer) which is understood to be the ratio of the speed of electromagnetic radiation in free space to the speed of the radiation in that material, with the radiation being of sodium yellow light at a wavelength of about 583.9 nanometers (nm). The refractive index can be measured using known methods and is generally measured using 20 an Abbe Refractometer.

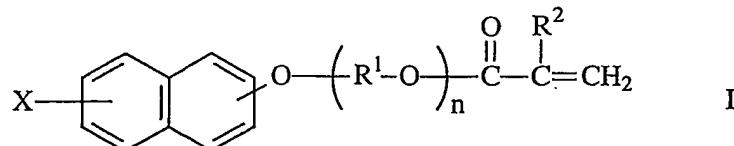
"Monomer" is defined herein as referring to a monomer on an individual scale, as well as referring collectively to a composition of such monomers on a macroscopic scale such that the composition can be described as having a physical state of matter (e.g. liquid, solid, etc.) and physical properties (e.g. melting point, viscosity, or refractive index).

25 "Melting point" refers to the temperature at which the monomer passes from a solid state to a liquid state, as measured at atmospheric pressure. The melting point can be measured, for example, using a Thomas-Hoover Melting Point Apparatus, from Thomas Scientific of Swedesboro New Jersey.

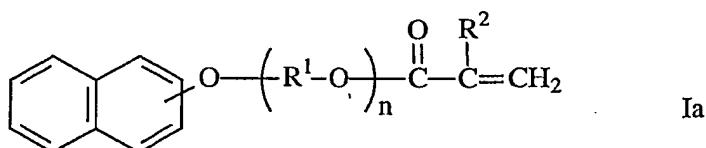
30 "Alkyl linking group" as used herein refers to a linear or branched, saturated or unsaturated hydrocarbon chain which chain can be interrupted by one or more heteroatoms such as nitrogen, oxygen or sulfur.

Monomer (a)

Monomer (a) is a naphthyl compound having the structure of the formula:

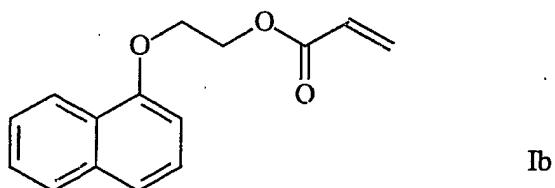


In this, X is hydrogen or one or more of methyl, chlorine, bromine or iodine, R¹ is a straight or branched alkyl linking group of 2 to 12 carbon atoms, R² is hydrogen or methyl, and n is 0 to 3. In a preferred embodiment, X is hydrogen, as seen in the formula:



More preferably, R¹ is ethylene, n is 1 and R² is hydrogen, as seen in the formula:

10

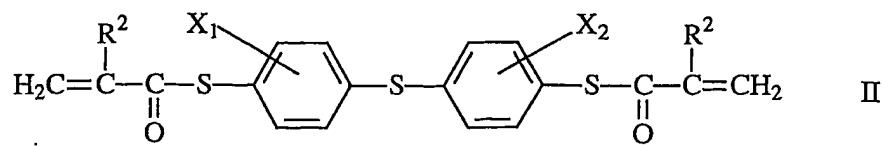


Preferably, the polymerizable compositions described by the present invention include 20 to 70 weight percent of monomer (a) and more preferably include about 30 to 15 50 weight percent of monomer (a).

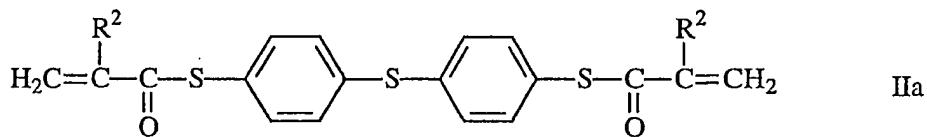
Monomer (b)

Monomer (b) is a diphenyl sulfide of the formula:

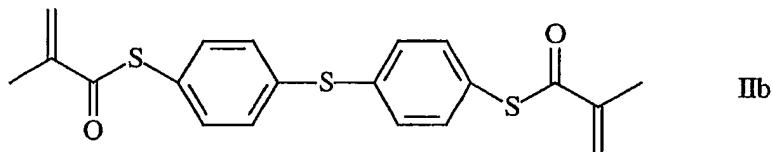
20



In this, X_1 and X_2 are each independently hydrogen or one or more of methyl, chlorine, bromine or iodine, and R^2 is hydrogen or methyl. In a preferred embodiment, X_1 and X_2 are each hydrogen, as in the formula:



More preferably, R^2 is methyl, as in the formula:



10 Preferably, the polymerizable compositions described by the present invention include 10 to 60 weight percent of monomer (b) and more preferably include about 15 to 30 weight percent of monomer (b).

Optional monomer

15 The compositions described by the present invention can include one or more optional monomers in addition to monomer (a) and monomer (b). The optional monomer or comonomer can be present at any useful concentration. For instance, the monomer or comonomer can be present in an amount as high as 70 weight percent. As expressed herein, weight percent refers to the fraction of a particular component in terms of the 20 entire composition.

25 The comonomer can include a combination of one or more monomers. Preferably, the comonomer includes monomers having high index of refraction values. In a preferred embodiment, the comonomer consists of one or more monomers each having an index of refraction of at least about 1.50. The comonomer can include a mixture of one or more (meth)acrylate monomers, including both mono-functional and multi-functional monomers. Useful brominated comonomers are described, for example, in U.S. Patent No. 5,932,626.

Typical multi-functional monomers include CN-104, CN-114, CN-115, CN-120, CN-975, CN112C60, SR-3368, SR-494, SR-399, and SR-9041, available from Sartomer Company, Exton, PA, Ebercyl 6700, 600, 3700, 3603, 3606, 6602, 4866, 1819, 830, 835, 693, 220, 9220 and RDX51027, available from UCB Chemicals Corp., Smyrna, GA, 5 RPC4482, AC-276, AC-440, and AC-890 available from Akros Chemicals, New Brunswick, NJ. Multi-functional monomers may include urethane acrylates, epoxy acrylates and polyester acrylates.

Multi-functional monomers can be used as crosslinking agents to increase the glass transition temperature of the polymer that results from the polymerizing of the 10 polymerizable composition. The glass transition temperature can be measured by methods known in the art, such as Differential Scanning Calorimetry (DSC), modulated DSC, or Dynamic Mechanical Analysis. Preferably the polymeric composition is crosslinked sufficiently to provide a glass transition temperature that is greater than 45°C.

Monomer compositions useful in this invention preferably have a melting point 15 that is below about 50°C. More preferably the monomer composition is a liquid at room temperature. Monomer compositions useful in this invention can be polymerized by conventional free radical polymerization methods.

Suitable methods of polymerization include solution polymerization, suspension polymerization, emulsion polymerization, and bulk polymerization. Additional suitable 20 methods include heating in the presence of a free-radical initiator, irradiation with electromagnetic radiation such as ultraviolet or visible light in the presence of a photoinitiator.

Alternatively, polymerization may include the use of photoinitiators such as, but not limited to, those available commercially from Ciba Geigy under the trade designations 25 DARACUR 1173, DAROCUR 4265, IRGACURE 651, IRGACURE 1800, IRGACURE 369, IRGACURE 1700, and IRGACURE 907. Phosphine oxide derivatives are preferred, such as LUCIRIN TPO, which is 2,4,6-trimethylbenzoyl diphenyl phosphine oxide, available from BASF, Charlotte, NC. The photoinitiator can be used at a concentration of about 0.1 to 10 weight percent. More preferably, the photoinitiator is a phosphine oxide 30 derivative used at a concentration of about 0.1 to 5 weight percent.

Other components

The polymerizable compositions described herein can also contain one or more other useful components that, as will be appreciated by those of skill in the art, can be useful in such a polymerizable composition. For example, the polymerizable composition 5 can include one or more surfactants, pigments, fillers, polymerization inhibitors, antioxidants, and other possible ingredients. Such components can be included in amounts known to be effective.

Surfactants such as fluorosurfactants can be included in the polymerizable 10 composition to reduce surface tension, improve wetting, allow smoother coating and fewer coating defects. Specific examples of useful surfactants include the nonionic fluorosurfactants available from 3M Company, St. Paul, MN under the tradenames FC-430, FC-171 and FC-740. These surfactants can be included in any useful amount, preferably between about 0.01 to about 0.3 weight percent.

Polymerizable beads, inorganic fillers and pigments can be added to the 15 polymerizable composition in order to improve processing, to impart slip and scratch resistance to the polymerized material, or to change the optical properties of the material. Examples of suitable beads include those made of polystyrene, polyacrylates, copolymers of styrene and acrylates, polyethylene, polypropylene, polytetrafluoroethylene and combinations thereof.

Examples of fillers and pigments include solid or hollow glass beads, silica, zirconia, aluminum trioxide, and titanium dioxide. The mean particle size can be between about 1 and 20 micrometers and the particles can be included in amounts ranging from about 0.25 to about 20 weight percent.

The polymerizable compositions can be used to prepare a variety of known and 25 useful high index of refraction optical products or articles, such as optical lenses and optical films such as high index of refraction films including microreplicated films such as totally internal reflecting films. Brightness enhancing films, flat films, multilayer films, retroreflective sheeting, and optical light fibers or tubes can also be made using the polymerizable compositions described herein. The production of optical products from 30 high index of refraction polymerizable compositions is described, for example, in U.S. Patent No. 4,542,449.

A preferred optical product that can be prepared from the polymerizable composition is a microstructure-bearing article. These can be constructed in a variety of forms, including those having a series of alternating tips and grooves sufficient to produce a totally internal reflecting film. An example of such a film is a brightness enhancing film 5 having a regular repeating pattern of symmetrical tips and grooves, while other examples have patterns in which the tips and grooves are not symmetrical. Preferred examples of microstructure bearing articles useful as brightness enhancing films are described by U.S. Patent Nos. 5,175,030 and 5,183,597.

According to these patents, a microstructure-bearing article can be prepared by a 10 method including the steps of (a) preparing a polymerizable composition; (b) depositing the polymerizable composition onto a master negative microstructured molding surface in an amount barely sufficient to fill the cavities of the master; (c) filling the cavities by moving a bead of the polymerizable composition between a preformed base and the master, at least one of which is flexible; and (d) curing the composition. The master can 15 be metallic, such as nickel, nickel-plated copper or brass, or can be a thermoplastic material that is stable under polymerization conditions and that preferably has a surface energy that permits clean removal of the polymerized material from the master.

A preferred embodiment of an optical product of the invention is illustrated in 20 Figure 1, which illustrates a microstructure-bearing brightness enhancing film. Referring to the Figure, the brightness enhancing film 30 includes a base layer 2 and a an optical layer 4. The optical layer 4 includes a linear array of regular right prisms, identified as 25 prisms 6, 8, 12 and 14. Each prism, for example prism 6, has a first facet 10 and a second facet 11. The prisms 6, 8, 12 and 14 are formed on a base 2 that has a first surface 18 on which the prisms are formed and a second surface 20 that is substantially flat or planar and opposite first surface 18.

By right prisms it is intended that the apex angle is typically about 90°, although this angle can range from about 70 to 120°, preferably between about 80 to 100°. Moreover, the prisms can have either sharp or rounded corners. The relationship between the total thickness 24 of the optical article, and the height 22 of the prisms is not critical, 30 although it is preferable to use relatively thinner optical layers with well-defined prism facets. The ratio of prism height 22 to total thickness 24 is preferably between about 25/50 and 25/125.

A brightness enhancement film, as is known in the art, can be positioned in a display panel between a diffuser and a display panel lit by a light source, e.g. a backlit liquid crystal display. The brightness enhancement film controls the exit angle of the light emitted from the light source, and increases the brightness of the display panel. The 5 increased brightness enables a sharper image to be produced by the display panel and allows the light source power to be reduced to produce a selected brightness.

The following non-limiting examples are intended only to illustrate the invention.

10

ExamplesMeasurement of Refractive Index

The refractive index of resin compositions and cured films were measured using an Abbe Refractometer, made by Erma Inc., of Tokyo Japan, and distributed by Fisher Scientific. The refractive index of cured films was measured using a Model 2010 Prism 15 Coupler from Metricon Corporation, Pennington, NJ.

Measurement of Brightness Gain

The brightness gain or "gain" is the ratio of photopic brightness of a backlit display (e.g., a liquid crystal display or LCD) with a brightness enhancing film (BEF) compared to 20 the photopic brightness of the display without the BEF (backlight only).

Photopic brightness with BEF

Photopic brightness without BEF

The brightness of a Sharp backlight model C12 P display, powered by a Hewlett Packard E3611A DC power supply was measured with and without BEF using a Minolta 25 Luminance Meter LS-100 Photometer. The BEF was placed on the backlight with the microfine prisms parallel to the long axis of the backlight, and facing the luminance meter. An acrylic frame was placed on top of the BEF to keep it flat against the backlight. After waiting for three minutes, the on-axis brightness of the display was measured in units of foot-lamberts. The BEF was then removed and the brightness was measured immediately 30 afterwards. The ratio of these two readings was reported as the gain.

Synthesis of 2-(1-naphthyloxy)-1-ethyl acrylate (1-NOEA):

A five liter three neck round bottom flask was equipped with a temperature probe, mechanical stirrer, and condenser. 400 grams 1-naphthol, 269 grams ethylene carbonate and 281 grams triethylamine were added to the flask. Using medium agitation, the batch
5 was heated to 95 °C and began to give off CO₂. The batch was held at this temperature for 12 hours, a sample was taken and residual 1-naphthol was determined by gas chromatography (GC). Heating of the batch continued at 95 °C until there was less than 3% residual 1-naphthol.

The reaction was then cooled to room temperature and 1470 grams tert-butyl
10 methyl ether and 56 grams triethylamine were added. 0.15 gram hydroquinone and 0.15 gram hydroquinone monomethyl ether were added as inhibitors. To the well-stirred reaction, 289 grams acryloyl chloride was added over a 2-4 hour period, keeping the batch temperature between 25-30 °C. The batch was stirred with medium agitation at room temperature for one hour after completing the addition. A sample was taken and GC run
15 to determine reaction completion (< 1% residual 2-(1-naphthyloxy)-1-ethanol).

The batch was then cooled to room temperature and then washed, first with 400 grams deionized water and 11 grams HCl, then with 250 grams of 15% sodium carbonate in water solution, and then with 250 grams of 20% sodium chloride solution. Residual solvent was removed using a rotary evaporator. The product was a dark colored, low
20 viscosity (<80 cps) liquid (570 g).

The crude monomer was purified using a continuous a high vacuum rolled film evaporator (available from UIC Inc. of Joliet, Illinois) with the following conditions: 110 °C jacket temperature, 30 °C condenser temperature, 40 °C feed temperature, 300 rpm rotor speed, and 1 micron vacuum. The distillation gave an 80-85% product split. The
25 product, 1-NOEA (475 grams), was a light yellow to orange liquid and was characterized by ¹³C NMR and confirmed to be >95% pure.

Examples 1-3

Polymerizable compositions were prepared by blending the ingredients in the
30 amounts shown in Table 1 in a 30 ml brown glass jar and heating the mixture to 70°C to melt the MPSMA (bis(4-methacryloyl thiophenyl sulfide available from Sumitomo Seika, Japan). The values for the monomers are the weight percent (wt%) of the component

based on the total weight of the composition. The values for the initiator, Daracure 4265 (available from Ciba-Geigy Corp, Hawthorne, NY), are parts per hundred parts polymerizable resin (phr).

Cured smooth films were prepared by placing the polymerizable composition
5 between a polyester film substrate (PET) and a smooth stainless steel master. The compositions were spread by means of a knife coater to give a coating of about 76 um thickness. The combination of PET substrate, polymerizable composition, and the master were passed under a UV lamp such that the polymerizable composition received a UV dose of about 1 J/cm². The PET and cured composition were then separated from the
10 smooth master. The refractive index of the cured film was measured and reported in Table 1.

Table 1

Example	1-NOEA (wt%)	MPSMA (wt%)	Daracure 4265 (phr)	Refractive Index
1	70	30	2	1.615
2	50	50	2	1.641
3	40	60	2	1.659

Examples 4-6

Polymerizable compositions were prepared by mixing 1-NOEA with RDX51027
15 (available from UCB Chemical Corp., Smyrna GA) and heating the mixture to 90°C for one hour until the RDX 51027 was completely melted. The MPSMA (in the amount shown in Table 2) was then added to the container and the entire mixture was heated at 70°C for one hour until the MPSMA had completely melted. The EB9220 (available from UCB Chemical Corp., Smyrna GA) and LUCERIN TPO photoinitiator (available from
20 BASF, Charlotte, NC) were then added and the mixture was heated at 65°C for 30 minutes until the TPO was completely melted. The values for the monomer in Table 2 are the weight percent (wt%) of the component based on the total weight of the composition. The values for the initiator, TPO, are parts per hundred parts polymerizable resin (phr).

Brightness enhancement films (BEFs) comprising a microstructured layer disposed
25 on a substrate were prepared by placing the polymerizable composition between a polyester (PET) substrate and a master tool having a micro-fine prismatic pattern. The

prism angle was 90 degrees, and the prism pitch was 50 um (micrometer) (90/50). The compositions were spread using a nip roll pressure of 2.1 kg/cm². The tool was heated to 54°C, 66°C and 43°C for examples 4, 5, and 6 respectively. The polymerizable composition was cured using UV radiation dose of about 1 J/cm². The brightness gain for these films was measured and is reported in Table 2.

Table 2

Example	1-NOEA (wt%)	MPSMA (wt%)	RDX51027 (wt%)	EB 9220 (wt%)	TPO (phr)	Gain
4	42	30	24	4	2.5	1.636
5	46	20	30	4	2.5	1.627
6	42	15	35	8	2.5	1.616

Examples 7 and 8

Polymerizable compositions were prepared by mixing NOEA with RDX51027 (in the amounts shown in Table 3) and heating the mixture to 90°C for one hour until the RDX 51027 was completely melted. The MPSMA (in the amount shown in Table 3) was then added to the container and the entire mixture was heated at 70°C for one hour until the MPSMA had completely melted. A third multifunctional component (CN-104 available from Sartomer Co., Exton, PA or AC-890 available from Akros Chemicals, New Brunswick, NJ) and TPO photoinitiator were then added and the mixture was heated at 65°C for 30 minutes until the TPO was completely melted. The values for the monomer in Table 3 are the weight percent (wt%) of the component based on the total weight of the composition. The values for the initiator, TPO, are parts per hundred parts polymerizable resin (phr).

Brightness enhancement films (BEFs) comprising a microstructured layer disposed on a substrate were prepared by placing the polymerizable composition between a polyester (PET) substrate and a master tool having a micro-fine prismatic pattern. The prism angle was 90 degrees, and the prism pitch was 50 um (micrometer) (90/50). The compositions were spread using a hand roller. The tool was heated to 54°C. The polymerizable composition was cured using a UV radiation dose of about 1 J/cm². The brightness gain for these films was measured and is reported in Table 3.

Table 3

Example	1- NOEA (wt%)	MPSMA (wt%)	RDX51027 (wt%)	CN- 104 (wt%)	AC- 890 (wt%)	TPO (phr)	Gain
7	55	35	5	5	0	2	1.648
8	55	35	5	0	5	2	1.652

Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims as set forth herein as follows.

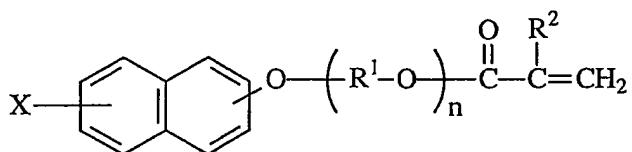
10

WE CLAIM:

1. A polymerizable composition comprising:

(a) a monomer of the formula

5



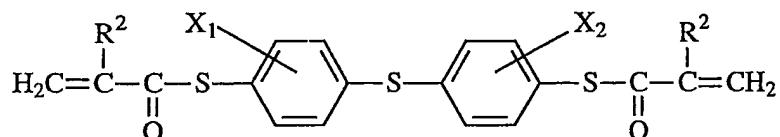
wherein X is hydrogen or one or more methyl, chlorine, bromine or iodine,

R¹ is a straight or branched alkyl linking group of 2 to 12 carbon atoms,

10 R² is hydrogen or methyl, and

n is 0 to 3; and

(b) a monomer of the formula



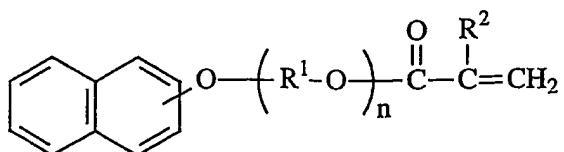
15

wherein X₁ and X₂ are each independently hydrogen or one or more methyl, chlorine, bromine or iodine, and

R² is hydrogen or methyl.

20

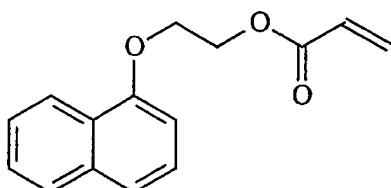
2. The composition of claim 1, wherein monomer (a) is of the formula



25 3. The composition of claim 1, wherein R¹ is a straight or branched linking group of 2 to 8 carbon atoms.

4. The composition of claim 1, wherein n is 1.
5. The composition of claim 1, wherein monomer (a) is of the formula

5

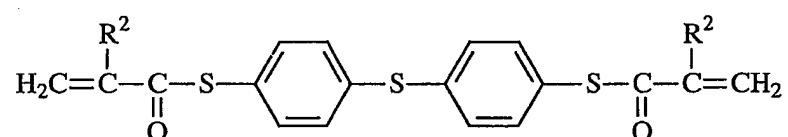


6. The composition of claim 1, comprising 20 to 70 weight percent of monomer (a).

10

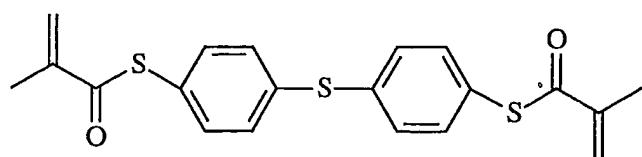
7. The composition of claim 1, comprising 30 to 50 weight percent of monomer (a).

15



9. The composition of claim 1, wherein monomer (b) is of the formula

20



10. The composition of claim 1, comprising 10 to 60 weight percent of monomer (b).

11. The composition of claim 1, comprising 15 to 30 weight percent of monomer (b).
12. The composition of claim 1, wherein an index of refraction of the
5 composition is at least 1.60.
13. The composition of claim 1, wherein a melting point of the composition is below 50°C.
10
14. The composition of claim 1, wherein the composition is a liquid at room temperature.
15
15. The composition of claim 1, which further comprises one or more multi-functional comonomers.
16. The composition of claim 15, comprising up to 50 wt-% of one or more multi-functional comonomers.
17. The composition of claim 15, wherein the comonomer has an index of
20 refraction of at least 1.50.
18. The composition of claim 1, further comprising a photoinitiator.
19. The composition of claim 18, wherein the photoinitiator comprises 2,4,6-trimethylbenzoyl diphenyl phosphine oxide.
25
20. A polymerized material comprising a composition of claim 1.
21. An optical product comprising:
30 a base (2); and
an optical layer (4) prepared from the polymerizable composition according to claim 1.

22. The optical product of claim 21, wherein the base is prepared from materials selected from the group consisting of cellulose acetate butyrate, cellulose acetate propionate, cellulose triacetate, polyether sulfone, polymethyl methacrylate, polyurethane, 5 polyester, polycarbonate, polyvinyl chloride, syndiotactic polystyrene, polyethylene naphthalate, copolymers or blends based on naphthalene dicarboxylic acids, and glass.
23. The optical product of claim 21, wherein the base (2) comprises a polarizer.
- 10 24. The optical product of claim 21, wherein the optical layer (4) comprises a microstructure-bearing layer.
25. The optical product of claim 21, wherein the optical product comprises a brightness enhancement film.
- 15 26. A lens sheet comprising:
a transparent substrate; and
an optical layer made from the polymerizable composition of claim 1.

20

1/1

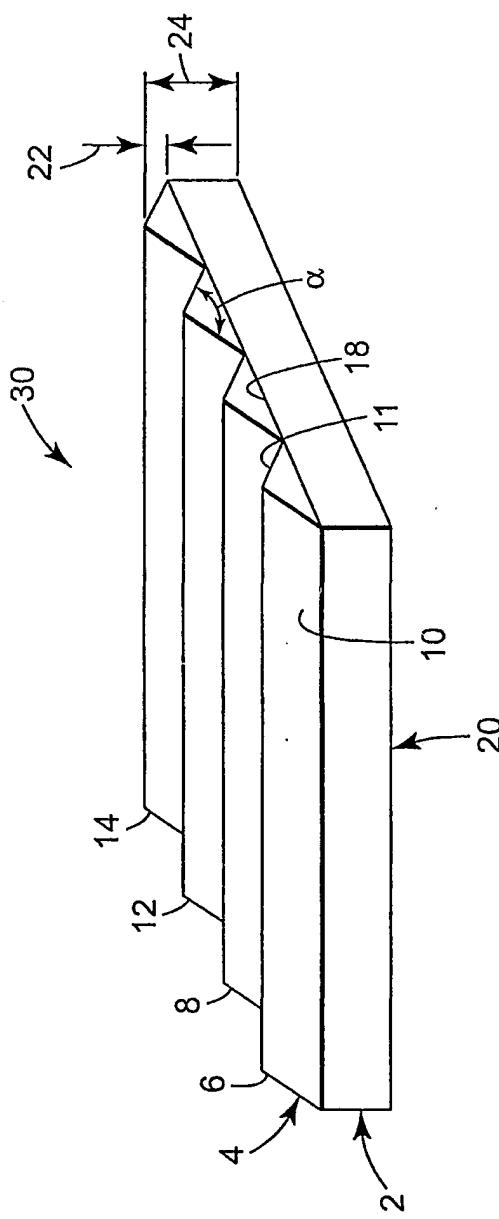


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/14040

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F228/02 C08F220/30 G02B1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 104, no. 4, 27 January 1986 (1986-01-27) Columbus, Ohio, US; abstract no. 20410, "PLASTIC LENSES WITH HIGH REFRACTIVE INDEXES." page 42; column 1; XP002183719 abstract & JP 60 144701 A (SHOWA DENKO K.K.) 31 July 1985 (1985-07-31) ----</p>	
A	<p>EP 0 745 621 A (ESSILOR INTERN.) 4 December 1996 (1996-12-04) ----</p>	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

22 November 2001

Date of mailing of the international search report

05/12/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx: 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Cauwenberg, C

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/14040

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
JP 60144701	A	31-07-1985	JP	1837143 C		11-04-1994
			JP	5044641 B		07-07-1993
EP 745621	A	04-12-1996	FR	2734828 A1		06-12-1996
			AU	705542 B2		27-05-1999
			AU	5456396 A		12-12-1996
			DE	69600238 D1		20-05-1998
			DE	69600238 T2		03-12-1998
			EP	0745621 A1		04-12-1996
			ES	2118008 T3		01-09-1998
			JP	9025321 A		28-01-1997
			US	6184323 B1		06-02-2001